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Comparison of Three Methods for Determining Total Alkalinity in Natural Waters

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Research Summary

Accurate determination of total alkalinity in natural water samples is a necessity for water quality surveys because it measures the acid neutralizing capacity of the water and is also used to determine if the water is saturated with carbonate minerals. In measuring total alkalinity in samples from 39 streams draining the Monitor, Toquima, and Toiyabe Ranges in central Nevada, three methods were used: (1) calculation from the difference between cations and strong acid anions (charge balance method); (2) titration with 0.02 M HCl to pH 4.5; and (3) the automated methyl orange colorimetric method (LACHAT QuikChem Method 10-303-31-1-A). All three methods gave comparable results, although the titration method gave slightly higher results than the other two. Calibration of the automated methyl orange colorimetric method is done by dividing the standard curve into three linear segments by the LACHAT QuikChem Method software. This calibration method gave comparable results to a nonlinear regression method for calculating alkalinity values from the nonlinear standard curve. All three methods gave the correct total alkalinity value (within the limits specified) of a USEPA standard. The automated methyl orange method appears suitable for determining total alkalinity in natural waters within the specified range of 10 to 300 mg/L total alkalinity as $CaCO_3$. Advantages of the method include a high degree of precision and accuracy and a high sample throughput rate. This last advantage greatly outweighs the much slower titration method.

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Total alkalinity is one of the more important factors routinely measured in surface and ground water quality surveys. It is a measure of the acid-neutralizing capacity (ANC) of the water and is the sum of all titratable bases (Stumm and Morgan 1981; Reuss and Johnson 1986; APHA and others 1992). In most natural waters bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) are the major species contributing to alkalinity. Thus, total alkalinity is often reported in units of mg/L as $CaCO_3$ or meq/L of total carbonate alkalinity. Hydroxyl, silicate, borate, phosphate, and dissolved organic carbon (DOC) concentrations in most natural fresh waters are normally too low to contribute significantly to alkalinity. However, in seawater, natural saline waters (such as desert playas), and some wastewaters, these species do contribute. For most natural waters alkalinity is given by

$$Alkalinity = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+] \quad (1)$$

where the brackets refer to molar concentrations.

There are several methods for determining total alkalinity in natural water samples, but titration with a standardized acid to a fixed end-point pH is the most common in routine use (APHA and others 1992). Ideally, the fixed end-point pH corresponds to the equivalence point of the bases present. When total alkalinity is due entirely to bicarbonate and carbonate species, the pH at the equivalence point of the titration is determined by the concentration of CO_2 at that point. The CO_2 concentration depends on the total carbonate species originally present and any losses that may have occurred during titration. For routine analysis of waters containing carbonate species, and perhaps other species that contribute to total alkalinity, an end-point pH of 4.5 is commonly used (APHA and others 1992).

Another method for determining total alkalinity is to calculate the difference between the sum of cations and the sum of strong acid anions (Reuss and Johnson 1986). This approach is based on charge balance and requires a complete analysis of all major cation and strong acid anion species. For most natural waters, the main cation species are H^+, Na^+, K^+, Mg^{2+}, and Ca^{2+}. The main anion species are OH^-, HCO_3^-, NO_3^-, SO_4^{2-}, F^-, and Cl^-. Other cation and anion species are usually present, but normally their concentrations are too low to contribute significantly to the charge balance. The charge balance for such a system is

$$[H^+] + [Na^+] + [K^+] + 2[Mg^{2+}] + 2[Ca^{2+}] = [OH^-] + [HCO_3^-] + [NO_3^-] + 2[SO_4^{2-}] + [F^-] + [Cl^-] \quad (2)$$

which rearranges to

$$[Na^+] + [K^+] + 2[Mg^{2+}] + 2[Ca^{2+}] - [NO_3^-] - 2[SO_4^{2-}] - [F^-] - [Cl^-] = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+] = \text{Alkalinity} \quad (3)$$

The right side of equation (3) is the same as equation (1). Thus, if the concentrations of the major cations and strong acid anions are measured, alkalinity can be computed by equation (3).

A third method for determining total alkalinity is the automated methyl orange colorimetric method developed recently by LACHAT Instruments (1992, QuikChem Method 10-303-31-1-A). In this method methyl orange is used as a color reagent because it changes color over the pH range of the equivalence point of the titration method. A methyl orange indicator solution is combined with a weak buffer at pH 3.1, which is just below the pH of its color change. When a sample containing alkalinity is reacted with the buffer and indicator, the methyl orange changes color in proportion to the change in pH of the weak buffer, and thus in proportion to the alkalinity of the sample. The applicable range of the method is 10 to 300 mg/L $CaCO_3$ with a method detection limit of about 3 mg/L $CaCO_3$ and a relative standard deviation of 0.9 percent at 100 mg/L $CaCO_3$. Turbidity and color interfere with the method, but colored samples can be diluted and turbid samples filtered to remove these interferences. The method has been approved by the U.S. Environmental Protection Agency and has therefore undergone extensive testing and evaluation.

Utah State University Analytical Labs recently purchased the total alkalinity module for their LACHAT flow injection analyzer. The Disturbed Land Rehabilitation Research Work Unit, U.S. Department of Agriculture Forest Service, frequently makes use of the Analytical Labs for analysis of water samples collected from various studies. Because it is desirable to use Environmental Protection Agency approved methods whenever possible, we decided to evaluate the automated methyl orange method for our needs by comparing it to the titration and charge balance methods. A water quality survey of streams draining Toiyabe National Forest lands in the Monitor, Toquima, and Toiyabe Ranges of central Nevada is being conducted as part of an ecosystem management research project. Stream water samples collected during this survey represent a wide range of total alkalinity levels and thus provided a representative set of natural waters for comparing the three methods for determining alkalinity.

Material and Methods

As part of an ecosystem management research project, a water quality survey of 39 streams draining the Monitor, Toquima, and Toiyabe Ranges of central Nevada was conducted in April and May 1994. Stream water temperature and pH were measured on site using an Orion Model SA250 portable pH meter, a Ross combination pH electrode, and an automatic temperature compensator. The meter and electrodes were calibrated with pH 4.00 and 7.00 buffers immediately prior to each pH and temperature measurement. Stream discharge was determined by measuring cross-sectional area and flow velocity using a Marsh-McBirney Model 201D portable water current meter (Gordon and others 1992). A grab sample of each stream was collected in a 500-mL plastic bottle.

On returning to the lab, all water samples were filtered through 0.4-um polycarbonate membrane filters. A 250-mL subsample of each was acidified with 1.25 mL of select-grade concentrated HNO_3. The remaining unacidified samples were stored at <4 °C and analyzed within 2 weeks of collection.

Unacidified samples were analyzed for NO_3+NO_2-N (LACHAT QuikChem Method 10-107-04-1-C), Cl (LACHAT QuikChem Method 10-117-07-1-C), and F (SPADNS method) (APHA and others 1992). Acidified samples were analyzed for Na, K, Mg, Ca, and S by inductively coupled plasma atomic emission spectrophotometry (ICPAES) (APHA and others 1992). For the charge balance calculations we assumed total S in the water samples determined by ICPAES was present as SO_4. This assumption is valid because these were well-oxidized surface waters.

Total alkalinity as ANC was calculated from the measured cation and strong acid anion concentrations using equation (3). Total alkalinity was also measured by titrating subsamples of the unacidified samples to pH 4.5 with 0.02 M HCl using an Orion Model EA 940 pH meter, a Ross combination pH electrode, and an automatic temperature compensator (Method 2320B.4.c.) (APHA and others 1992) and by the automated methyl orange colorimetric method (LACHAT QuikChem Method 10-303-31-1-A). Duplicate samples were analyzed by the automated methyl orange method. A new calibration curve was prepared for each duplicate run.

Reagents and standards for the automated methyl orange method were prepared as follows. A pH 3.1, 25.0 mM potassium acid phthalate buffer was prepared by dissolving 2.55 g of potassium acid phthalate in 450 mL of deionized water, adding 45.0 mL of standardized 0.1 M HCl to bring the pH to 3.1, and diluting to 500 mL with deionized water in a volumetric flask. Methyl orange indicator solution was prepared by dissolving 87.5 mg of methyl orange in 500 mL of deionized water in a volumetric flask. A 1,000 mg/L as $CaCO_3$ standard was prepared by dissolving 0.530 g of anhydrous primary reagent grade Na_2CO_3 in 500 mL of deionized water in a volumetric flask. Working standards of 10, 30, 50, 100, and 300 mg/L as $CaCO_3$ were prepared by diluting 1.00, 3.00, 5.00, 10.0, and 30.0 mL of the 1,000 mg/L as $CaCO_3$ standard to 100 mL with deionized water in a series of volumetric flasks.

Results and Discussion

The streams sampled, sample locations, sampling dates, discharge, temperature, and pH measured in the field are listed in table 1. The results of this water quality survey and possible implications for ecosystem management in the Great Basin will be discussed elsewhere. This paper focuses only on evaluating the three methods of determining total alkalinity.

Standard calibration curves for two different runs by the automated methyl orange method are shown in figure 1. The curves are slightly nonlinear and a second-order regression gave an excellent fit to the data. However, the LACHAT software does not compute nonlinear regressions for standard curves. Instead, the software divides the standard curve into a series of linear segments and a linear regression is calculated for each segment. These segments are 300 to 100 mg/L as $CaCO_3$, 100 to 10 mg/L as $CaCO_3$, and 10 to 0 mg/L as $CaCO_3$. Calibration statistics for these linear segments of the standard curves are shown in table 2. The third segment from 10 to 0 mg/L as $CaCO_3$ gave the lowest r value and highest standard deviation of the slope for all three segments, but this segment is also outside the recommended range of the method.

Table 1—Sample locations, sampling dates, discharge, temperature, and pH of streams in the Monitor, Toquima, and Toiyabe Ranges of central Nevada.

Stream	Location	Date	Discharge	Temp.	pH
			m^3/s	*°C*	
Monitor Range					
Faulkner Creek	Road crossing	4/23/94	0.0139	7.8	7.68
Allison Creek	FR004 crossing	4/21/94	0.0164	11.6	7.89
Clear Creek	Mouth of canyon	4/22/94	0.0181	12.1	8.37
Danville Creek	FR139 crossing	4/22/94	0.0016	14.4	8.55
Willow Creek (south)	Below ranch	4/22/94	0.0129	12.6	8.23
Barley Creek	FR005 crossing	4/22/94	0.1382	12.8	7.96
Mosquito Creek	Trailhead	4/23/94	0.0303	4.7	7.77
Morgan Creek	NF boundary	4/23/94	0.0079	7.8	7.5
Willow Creek (west)	NF boundary	4/23/94	0.0006	10.4	8.31
Reynolds Creek	Below ranch	4/23/94	0.0148	6.4	7.95
Toquima Range					
Stoneberger Creek	FR138 crossing	5/5/94	0.0005	12.3	8.46
Pine Creek	Campground	5/6/94	0.0845	6.1	7.77
Andrews Creek	Road crossing	5/6/94	0.0139	8.2	7.85
Meadow Creek	FR208 crossing	5/6/94	0.0553	9.9	8.72
Shoshone Creek	NF boundary	5/6/94	0.0284	6.9	7.42
Jefferson Creek	NF boundary	5/6/94	0.1693	8.1	7.61
Willow Creek	Road crossing	5/6/94		7.8	7.61
Barker Creek	Road crossing	5/6/94	0.0558	6.3	7.32
Toiyabe Range					
Birch Creek	Mouth of canyon	5/19/94	0.2061	8.0	8.63
Lynch Creek	Road crossing	5/20/94	0.0266	6.6	8.08
Tar Creek	NF boundary	5/20/94	0.0680	7.6	8.16
Kingston Creek	Guard station	5/21/94	0.1799	11.1	8.17
Bowman Creek	Road crossing	5/21/94	0.1504	9.0	8.45
Aiken Creek	End of road	5/21/94	0.0390	4.8	7.94
Alice Gendron Creek	NF boundary	5/21/94	0.0582	6.2	7.84
Summit Creek	Road crossing	5/8/94	0.0117	6.1	7.86
Ophir Creek	Mouth of canyon	5/8/94	0.0772	6.0	7.85
Last Chance Creek	End of road	5/8/94	0.0430	6.1	7.96
North Twin River	Dam	5/8/94		6.5	7.92
South Twin River	Dam	5/8/94		7.4	7.94
Jett Creek	Mouth of canyon	5/8/94	0.1092	8.3	8.01
Reese River	FR016 crossing	5/20/94		16.3	8.12
Stewart Creek	FR119 crossing	5/7/94	0.0600	3.0	7.54
Clear Creek	Upper end of ranch	5/7/94	0.1327	5.7	7.44
Marysville Creek	Road crossing	5/7/94	0.0952	4.2	8.02
Tierney Creek	Road crossing	5/7/94	0.1135	6.4	7.82
Cottonwood Creek	Below confluence	5/20/94	0.3905	5.6	7.97
Washington Creek	FR126 crossing	5/20/94	0.1708	8.3	8.03
Big Creek	Campground	5/20/94	0.4994	9.8	8.11

To compare the two methods of computing the calibration curve, predicted $CaCO_3$ concentrations and residuals were calculated for the standards using the nonlinear and linear segment regressions (table 3). For nonlinear regression, the second-order regression equations shown in figure 1 were used to calculate the predicted $CaCO_3$ concentrations from the measured absorbencies of the standards. For linear segment regression, predicted $CaCO_3$ concentrations were computed by the LACHAT software. The results indicate that either method is satisfactory.

Both nonlinear and linear segment calibration curves were also used to calculate total alkalinity as $CaCO_3$ in the stream samples (table 4). Total alkalinity was calculated from the measured sample absorbencies using the regression equations in figure 1 and the LACHAT software output total alkalinity

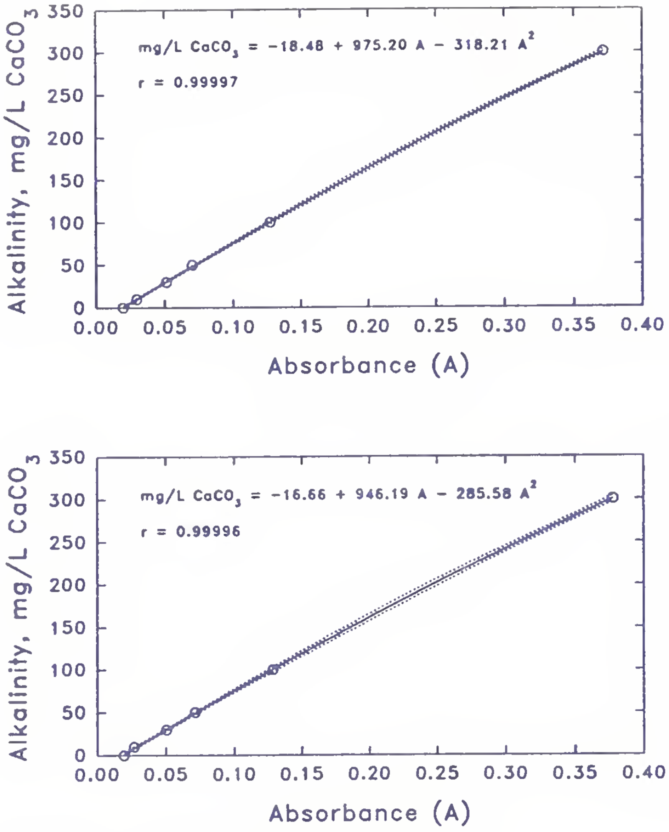

Figure 1—Standard curves for two-sample analysis runs by the automated methyl orange method. The solid line is the nonlinear regression and the dashed lines represent the 95 percent confidence interval about the regression line.

Table 2—Calibration statistics for the linear segments of the standard curves; r is the correlation coefficient and SD is the standard deviation of the slope.

Segment	Range	Curve 1 r	Curve 1 SD	Curve 2 r	Curve 2 SD
	mg/L $CaCO_3$		*Percent*		*Percent*
1	300-100	0.9997	1.2	0.9999	0.5
2	100-10	0.9975	2.0	0.9990	1.3
3	10-0	0.9416	17.6	0.8720	27.1

values of the samples directly from the linear segment regressions. Both calibration methods gave comparable results, although nonlinear regression gave slightly higher values at the higher alkalinity levels. These differences are too small, however, to be of practical significance.

Total alkalinity as $CaCO_3$ by the automated methyl orange method (using linear segment calibration) was plotted against total alkalinity as $CaCO_3$ by the titration method and a regression line was computed to directly compare the two methods for the stream samples (fig. 2). The titration method tended to give slightly higher results, as evidenced by an intercept of less than 0 (−2.21) and a slope slightly less than one (0.98 ± 0.01), but differences between the two methods are relatively minor and are of no practical significance.

The water analysis data needed to compute total alkalinity as ANC by equation (3) are listed in table 5. In addition, total alkalinity as ANC by the titration method was used along with the data in table 5 to calculate an ion balance as a check of analysis completeness (table 6). These results indicate that all the major ions were accurately accounted for by the water analysis, although the sum of anions was slightly greater than the sum of cations for all samples. There was a small bias in the analyses. This was probably the result of the tendency of the titration

Table 3—Predicted $CaCO_3$ concentrations and residuals of the standards for the automated methyl orange method from nonlinear and linear segment regression analysis.

	Nonlinear regression				Linear segment regression			
	Curve 1		Curve 2		Curve 1		Curve 2	
True $CaCO_3$	Predicted $CaCO_3$	Residual[1]	Predicted $CaCO_3$	Residual	Predicted $CaCO_3$	Residual	Predicted $CaCO_3$	Residual
mg/L	*mg/L*	*Percent*	*mg/L*	*Percent*	*mg/L*	*Percent*	*mg/L*	*Percent*
300	300.0	−0.01	300.0	−0.01	300.0	0.00	300.0	0.00
100	100.7	0.69	100.4	0.38	100.0	0.00	100.0	0.00
50	48.4	−3.18	49.4	−1.30	48.0	−4.00	49.3	−1.40
30	30.6	2.05	30.4	1.31	30.6	2.00	30.8	2.67
10	10.0	0.11	8.4	−16.00	10.6	6.00	10.0	0.00
0	0.3		1.5		0.0		0.0	

[1] (True value-Predicted value)/(True value) x 100.

Table 4—Mean ± standard error (SE) for duplicate analyses of total alkalinity as $CaCO_3$ in streams in the Monitor, Toquima, and Toiyabe Ranges as calculated from the calibration curves using nonlinear and linear segment regression.

Stream	Nonlinear regression Mean ± SE $CaCO_3$	Linear segment regression Mean ± SE $CaCO_3$
	mg/L	
Monitor Range		
Faulkner Creek	31.8 ± 0.5	32.0 ± 0.7
Allison Creek	43.5 ± 1.6	43.4 ± 1.7
Clear Creek	173.2 ± 0.4	168.7 ± 0.2
Danville Creek	207.4 ± 0.1	202.6 ± 0.3
Willow Creek (south)	144.5 ± 1.6	141.2 ± 1.3
Barley Creek	33.5 ± 2.0	33.7 ± 1.6
Mosquito Creek	32.9 ± 4.1	33.1 ± 4.2
Morgan Creek	40.0 ± 1.7	40.0 ± 1.8
Willow Creek (west)	141.0 ± 3.0	137.8 ± 2.7
Reynolds Creek	52.8 ± 3.6	52.5 ± 3.7
Toquima Range		
Stoneberger Creek	129.5 ± 1.3	127.0 ± 1.0
Pine Creek	27.8 ± 0.2	28.1 ± 0.1
Andrews Creek	31.5 ± 0.5	31.7 ± 0.3
Meadow Creek	169.2 ± 2.4	164.9 ± 2.5
Shoshone Creek	48.5 ± 2.5	48.3 ± 2.3
Jefferson Creek	50.9 ± 2.3	50.8 ± 2.1
Willow Creek	79.9 ± 1.5	79.5 ± 1.4
Barker Creek	34.5 ± 0.1	34.6 ± 0.3
Toiyabe Range		
Birch Creek	171.7 ± 0.2	167.3 ± 0.0
Lynch Creek	141.8 ±12.3	138.6 ±11.5
Tar Creek	171.4 ± 0.4	167.0 ± 0.6
Kingston Creek	207.3 ± 4.6	202.5 ± 4.5
Bowman Creek	146.8 ± 0.2	143.3 ± 0.1
Aiken Creek	42.0 ± 0.5	41.9 ± 0.6
Alice Gendron Creek	48.3 ± 1.5	48.1 ± 1.6
Summit Creek	171.2 ± 0.5	166.9 ± 0.3
Ophir Creek	92.6 ± 0.5	92.4 ± 0.6
Last Chance Creek	106.7 ± 2.8	105.8 ± 2.8
North Twin River	44.9 ± 2.0	44.8 ± 1.8
South Twin River	51.7 ± 0.1	51.5 ± 0.3
Jett Creek	59.7 ± 1.9	59.4 ± 1.8
Reese River	166.8 ± 1.5	162.6 ± 1.3
Stewart Creek	20.4 ± 1.8	21.0 ± 2.0
Clear Creek	21.0 ± 2.9	21.6 ± 3.1
Marysville Creek	138.6 ± 0.7	135.5 ± 0.9
Tierney Creek	80.5 ± 1.7	80.2 ± 1.6
Cottonwood Creek	56.6 ± 0.1	56.3 ± 0.2
Washington Creek	101.6 ± 0.3	101.6 ± 0.4
Big Creek	214.8 ± 4.2	210.1 ± 4.0

method to give slightly higher results than the automated methyl orange or charge balance methods.

Total alkalinity values (meq/L of ANC) for the stream water samples by all three methods are presented in table 7. The smallest differences between results were found with the charge balance and automated methyl orange methods. The results by the automated methyl orange method listed in this table were computed using linear segment calibration. The titration method gave slightly higher values, as already discussed, and this may be related to the sharpness of the end-point of the titration. Methods are available to improve the accuracy of the titration method (Stumm and Morgan 1981), but given the close correspondence between the methods, additional improvements in the titration method are

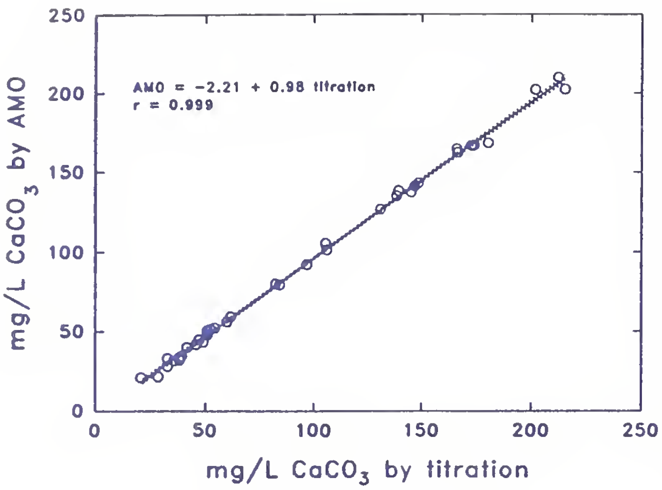

Figure 2—Comparison of total alkalinity as $CaCO_3$ by the automated methyl orange (AMO) method and the titration method. The solid line is the linear regression and the dashed lines represent the 95 percent confidence intervals about the regression line.

Table 5—Major cation and strong acid anion concentrations in streams in the Monitor, Toquima, and Toiyabe Ranges of central Nevada. These data were used to calculate total alkalinity as ANC in table 7 using equation (3).

Stream	Na	K	Mg	Ca	$NO_3 + NO_2$	SO_4	F	Cl
				mM				
Monitor Range								
Faulkner Creek	0.339	0.0256	0.0489	0.206	0.00942	0.0592	0.00895	0.0750
Allison Creek	0.368	0.0512	0.0543	0.284	0.00935	0.0499	0.00632	0.0798
Clear Creek	0.304	0.0256	0.436	1.50	0.00314	0.337	0.00947	0.0857
Danville Creek	0.611	0.0512	1.04	1.44	0.00300	0.686	0.0221	0.125
Willow Creek (south)	0.826	0.102	0.378	1.22	0.00607	0.527	0.0137	0.198
Barley Creek	0.311	0.0256	0.0489	0.209	0.00707	0.0530	0.00789	0.0654
Mosquito Creek	0.288	0.0256	0.0609	0.154	0.00300	0.0437	0.00895	0.0685
Morgan Creek	0.372	0.0256	0.0456	0.245	0.00528	0.0717	0.0105	0.0699
Willow Creek (west)	0.901	0.256	0.295	0.865	0.00400	0.184	0.0142	0.258
Reynolds Creek	0.420	0.0512	0.0892	0.315	0.00243	0.0842	0.00737	0.120
Toquima Range								
Stoneberger Creek	0.766	0.102	0.422	0.992	0.00257	0.458	0.0147	0.242
Pine Creek	0.271	0.000	0.0358	0.170	0.00642	0.0281	0.00368	0.0448
Andrews Creek	0.316	0.0256	0.0415	0.178	0.00385	0.0437	0.00684	0.0575
Meadow Creek	1.021	0.154	0.268	1.19	0.00678	0.312	0.0263	0.200
Shoshone Creek	0.441	0.0256	0.0625	0.360	0.00678	0.122	0.0253	0.104
Jefferson Creek	0.407	0.0256	0.0711	0.341	0.00385	0.112	0.0137	0.0581
Willow Creek	0.681	0.0256	0.0913	0.494	0.00407	0.0842	0.00895	0.136
Barker Creek	0.296	0.000	0.0522	0.215	0.00228	0.0405	0.00737	0.0561
Toiyabe Range								
Birch Creek	0.347	0.0512	0.762	1.37	0.00542	0.558	0.0179	0.0953
Lynch Creek	0.168	0.0512	0.239	1.13	0.00671	0.128	0.00526	0.0415
Tar Creek	0.110	0.0256	0.455	1.26	0.00535	0.0998	0.00263	0.0338
Kingston Creek	0.162	0.0256	0.959	1.30	0.0101	0.408	0.0105	0.0460
Bowman Creek	0.131	0.0256	0.148	1.32	0.00692	0.0967	0.00526	0.0367
Aiken Creek	0.153	0.0256	0.0641	0.341	0.00271	0.0499	0.00474	0.0285
Alice Gendron Creek	0.138	0.0256	0.122	0.329	0.00685	0.0405	0.00579	0.0262
Summit Creek	0.239	0.0512	0.661	1.32	0.00328	0.443	0.00895	0.0564
Ophir Creek	0.156	0.0256	0.271	0.683	0.00278	0.118	0.00579	0.0446
Last Chance Creek	0.152	0.0256	0.352	0.749	0.00171	0.165	0.00737	0.0448
North Twin River	0.212	0.0256	0.0806	0.307	0.00542	0.0468	0.00579	0.0400
South Twin River	0.238	0.0256	0.0489	0.383	0.00450	0.0499	0.00947	0.0446
Jett Creek	0.228	0.000	0.112	0.486	0.00200	0.112	0.00474	0.0392
Reese River	1.244	0.128	0.318	0.945	0.00692	0.218	0.0221	0.215
Stewart Creek	0.194	0.0256	0.247	0.0881	0.00421	0.0218	0.00474	0.0361
Clear Creek	0.247	0.0256	0.0403	0.138	0.00514	0.0405	0.00632	0.0451
Marysville Creek	0.252	0.0256	0.649	0.789	0.00621	0.221	0.00526	0.0598
Tierney Creek	0.429	0.0512	0.245	0.636	0.00278	0.274	0.0126	0.0857
Cottonwood Creek	0.213	0.0512	0.144	0.487	0.00614	0.143	0.00684	0.0460
Washington Creek	0.194	0.0256	0.127	0.905	0.00535	0.106	0.00737	0.0375
Big Creek	0.186	0.0256	1.06	1.39	0.00778	0.483	0.0121	0.0508

Table 6—Cation-anion balance in streams in the Monitor, Toquima, and Toiyabe Ranges of central Nevada.

Stream	Cations[1]	Anions[2]	Ion balance[3]	Ion balance[4]
	meq/L			*Percent*
Monitor Range				
Faulkner Creek	0.876	0.986	–0.110	5.91
Allison Creek	1.097	1.182	–0.085	3.73
Clear Creek	4.197	4.379	–0.182	2.12
Danville Creek	5.619	5.821	–0.202	1.77
Willow Creek (south)	4.119	4.208	–0.089	1.07
Barley Creek	0.855	0.960	–0.105	5.79
Mosquito Creek	0.744	0.826	–0.082	5.24
Morgan Creek	0.981	1.073	–0.092	4.48
Willow Creek (west)	3.484	3.555	–0.071	1.01
Reynolds Creek	1.283	1.385	–0.102	3.84
Toquima Range				
Stoneberger Creek	3.702	3.807	–0.105	1.40
Pine Creek	0.683	0.769	–0.086	5.91
Andrews Creek	0.781	0.864	–0.083	5.06
Meadow Creek	4.019	4.190	–0.099	1.19
Shoshone Creek	1.314	1.397	–0.083	3.04
Jefferson Creek	1.259	1.319	–0.059	2.30
Willow Creek	1.880	2.007	–0.127	3.27
Barker Creek	0.832	0.936	–0.104	5.88
Toiyabe Range				
Birch Creek	4.659	4.716	–0.057	0.61
Lynch Creek	2.959	3.096	–0.137	2.27
Tar Creek	3.577	3.684	–0.107	1.48
Kingston Creek	4.722	4.919	–0.197	2.04
Bowman Creek	3.100	3.209	–0.110	1.74
Aiken Creek	0.991	1.054	–0.063	3.07
Alice Gendron Creek	1.067	1.136	–0.070	3.17
Summit Creek	4.268	4.414	–0.146	1.69
Ophir Creek	2.092	2.225	–0.133	3.08
Last Chance Creek	2.382	2.500	–0.117	2.41
North Twin River	1.014	1.080	–0.066	3.13
South Twin River	1.129	1.208	–0.079	3.38
Jett Creek	1.427	1.501	–0.074	2.52
Reese River	3.903	4.019	–0.116	1.46
Stewart Creek	0.446	0.499	–0.053	5.61
Clear Creek	0.630	0.713	–0.083	6.21
Marysville Creek	3.156	3.286	–0.130	2.03
Tierney Creek	2.245	2.291	–0.046	1.01
Cottonwood Creek	1.527	1.543	–0.016	0.52
Washington Creek	2.288	2.377	–0.089	1.92
Big Creek	5.113	5.286	–0.173	1.66

[1] Cations, meq/L = $[Na^+] + [K^+] + 2[Mg^{2+}] + 2[Ca^{2+}]$.
[2] Anions, meq/L = Alkalinity (titration) + $[NO_3^- + NO_2^-] + 2[SO_4^{2-}] + [F^-] + [Cl^-]$.
[3] Ion balance, meq/L = Cations – Anions.
[4] Ion balance, percent = (Cations – Anions)/(Cations + Anions) x 100.

unnecessary for routine analyses in the range of alkalinities used in this study.

As a final check of the titration and automated methyl orange methods, a USEPA minerals standard was analyzed by both methods. The true alkalinity value for this standard was given as 21.4 mg/L as $CaCO_3$ with a 95 percent confidence interval of 17.5 to 24.5 mg/L as $CaCO_3$. The titration method gave a value of 23.2 mg/L as $CaCO_3$ and the automated methyl orange method gave a mean value of 22.6 mg/L as $CaCO_3$ with a standard error of 0.8 mg/L for nine replicate analysis distributed over the two sample

Table 7—Total alkalinity as ANC in streams in the Monitor, Toquima, and Toiyabe Ranges of central Nevada by the charge balance, titration, and automated methyl orange methods.

Stream	Charge balance	Titration	Automated methyl orange
	ANC, meq/L		
Monitor Range			
Faulkner Creek	0.664	0.764	0.640
Allison Creek	0.902	0.980	0.868
Clear Creek	3.426	3.606	3.374
Danville Creek	4.097	4.302	4.051
Willow Creek (south)	2.848	2.934	2.823
Barley Creek	0.668	0.764	0.673
Mosquito Creek	0.576	0.654	0.661
Morgan Creek	0.751	0.832	0.799
Willow Creek (west)	2.840	2.902	2.755
Reynolds Creek	0.984	1.086	1.050
Toquima Range			
Stoneberger Creek	2.525	2.616	2.539
Pine Creek	0.572	0.654	0.561
Andrews Creek	0.626	0.712	0.634
Meadow Creek	3.235	3.320	3.297
Shoshone Creek	0.935	1.016	0.966
Jefferson Creek	0.959	1.020	1.015
Willow Creek	1.563	1.682	1.590
Barker Creek	0.685	0.784	0.691
Toiyabe Range			
Birch Creek	3.424	3.480	3.346
Lynch Creek	2.650	2.784	2.771
Tar Creek	3.335	3.450	3.340
Kingston Creek	3.838	4.034	4.049
Bowman Creek	2.858	2.970	2.865
Aiken Creek	0.855	0.916	0.837
Alice Gendron Creek	0.947	1.018	0.962
Summit Creek	3.313	3.464	3.337
Ophir Creek	1.802	1.936	1.848
Last Chance Creek	1.998	2.110	2.115
North Twin River	0.869	0.942	0.896
South Twin River	0.971	1.048	1.029
Jett Creek	1.157	1.232	1.188
Reese River	3.222	3.330	3.251
Stewart Creek	0.357	0.414	0.420
Clear Creek	0.492	0.568	0.432
Marysville Creek	2.642	2.766	2.710
Tierney Creek	1.595	1.646	1.603
Cottonwood Creek	1.181	1.198	1.126
Washington Creek	2.025	2.122	2.032
Big Creek	4.076	4.240	4.201

runs. Both methods are within the 95 percent confidence interval specified for this standard even at this relatively low alkalinity level.

The results of this study show that the automated methyl orange method gives accurate total alkalinity values with good precision for natural water as $CaCO_3$) of alkalinities. For low levels of alkalinity (<10 mg/L as $CaCO_3$), alternative methods such as Gran-plot titration should be used (APHA and others 1992; Stumm and Morgan 1981).

Sample throughput is high with the automated methyl orange method. Up to 180 samples per hour can be analyzed, exclusive of the time required to analyze check standards and re-calibrate if necessary.

The titration method is much slower even when an autotitrator is used. Of course, reagent preparation and instrument setup time must be considered. With small numbers of samples, the titration method may be faster. The charge balance method requires a complete and accurate analysis of the water sample, which can be time consuming. Normally, this is required for most water quality surveys, so it can serve as a check of the titration or methyl orange methods.

The automated methyl orange method also has several convenient quality control features that help validate the results. Limits on the calibration statistics can be set to accept or reject the calibration curve. Check standards can be analyzed at user set intervals and re-calibration can be required if the results exceed user set limits for the check standards. Given the high sample throughput, quality control features, and demonstrated accuracy and precision, the automated methyl orange method is preferred for routine determination of total alkalinity in water quality surveys.

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Three methods were used for determining total alkalinity in natural waters: (1) calculation from the difference between cations and strong acid anions (charge balance method); (2) titration with 0.02 N HCl to pH 4.5; and (3) the automated methyl orange colorimetric method. All three methods gave comparable total alkalinity values for 39 stream water samples collected from the Monitor, Toquima, and Toiyabe Ranges from central Nevada. The automated methyl orange method is precise and accurate and has an added advantage of a high sample throughput rate compared to the slower titration method.

Keywords: methyl orange colorimetric, titration, charge balance

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